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Compression-Induced Electrical Percolation and Enhanced Mechanical properties of Polydimethylsiloxane-Based Nanocomposites

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Abstract: In this work, a compression-induced percolation threshold was found when the thickness of polydimethylsiloxane (PDMS) nanocomposite samples was reduced via a Spatial Confining Forced Network Assembly (SCFNA) process from 1.0 mm to 0.1 mm. Such as for PDMS/ 2 wt% short carbon fiber (SCF)/4 wt% carbon nanotube (CNT) composite, its conductivity was more than 8 times enhanced to 487 S/m from 59.5 S/m, and the mechanical properties of composites have been improved by more than 15% accordingly. Comparatively, when increased the concentration of CNT or Gr from 1 wt% to 4 wt%, the electrical conductivity of PDMS nanocomposites at 1 mm thickness was barely changed as it generally reached saturation and became independent of filler loading. Compared with the traditional blending method, it indicates that the SCFNA process can further promote the maximum electrical conductivity of polymer nanocomposites when the filler concentration has little effect on the conductivity. Especially under the condition of relatively high filler concentration, the electrical conductivity enhancement effect becomes more significant, that is contrary to the classical percolation theory. Moreover, the mechanical properties of the nanocomposites can be slightly improved by the mechanical compression, which make it more suitable for flexible electronics devices applications.

Keywords: electrical percolation; enhanced mechanical properties; forced compression; nanocomposites; hierarchical micro-/nanoscale filler

1. Introduction

The nanocomposites with ultra-high electrical conductivity and mechanical flexibility have become a great concern of polymer engineers and researchers, as they may primarily contribute to the development of highly sensitive flexible sensor technology [1-12], especially the flexible electronic skin technology proposed by American professor Zhenan Bao [13-18] and some multifunctional ultrasensitive strain sensors with self-cleaning [8,9] or self-healing capability [10] reported by Zhanhu Guo. However, the moderate conductivity of polymer/carbon nanocomposites, which electrical conducting behavior follows the percolation model [19], has severely constrained their applications. In particular, intelligent wearable flexible sensing materials and flexible electrodes, extensively-used techniques require higher electrical conductivity and meet mechanical properties. Flexible conductive polymer composites (CPCs) can be composed of conductive fillers and flexible insulating polymer, which has the advantages of easy processing and stable performance under natural conditions [20-24]. However, the addition of conductive fillers in the insulating polymer can only improve the conductivity to a limited extent because of the insulating polymer barrier effect on the conductive network [25-27]. Excessive addition of conductive filler can't improve the electrical conductivity of the composite, but significantly reduce its mechanical properties [28-30].

In order to prepare a relatively high electrically conductive nanocomposite in a lower percolation threshold, various methods such as in situ polymerization [31-32] or else forming segregated microstructures [33-35], have been used to give full paly to conductive effect of the functionally dispersed phase fillers. Yu et al [35] proposed a vacuum-assisted layer-by-layer assembly technique to deposit electrically conductive silver nanowires (AgNWs) on textiles as the highly conductive skeleton. The flexible and multifunctional textile exhibits a low sheet resistance of 0.8 Ω sq^{-1}. Thus, nanocomposites with both electrical and mechanical properties were obtained. Guo et al [36] reported a cracked cellulose nanofibril/silver nanowire (CA) layer-coated polyurethane (PU) sponge through a simple dip-coating process followed by precompression treatment. due to the excellent electrical conductivity, the sponge exhibited the capability of detecting both small and large motions over a wide compression strain range of 0−80%. Based on the "crack effect", the sensor possessed a detection limit as low as 0.2%. Another flexible conductive thermoplastic polyurethane (TPU)/ carbon black foam with an intriguing pinnate-veined aligned porous was prepared by a unidirectional freeze-drying process, as the CB particles are uniformly dispersed in the skeleton of the as-prepared foam, it results in a low percolation threshold of 0.48 vol.% [37]. According to the report [38], as to the effect of the selective location of graphene in the polyurethane(TPU) phase rather than in the polypropylene(PP) phase, the electrically conductive TPU/PP/ graphene nanocomposites with a low percolation threshold of 0.054 wt% was prepared by solution-flocculation and melt-mixing process using a micron twin-screw extruder. In addition to that, Changyu Shen et al produced a thermoplastic polyurethane (TPU) fiber through a scalable and facile strategy by wet-spinning and ultra-sonication, as to the conductive MWCNTs network decorated on the TPU fibers surface, the TPU fibers exhibit extremely high electrical conductivity and tensile properties [39]. It can be seen that the construction of conductive filler network on the surface of flexible matrix by dip-coating or wet-spinning is an effective method to improve the conductivity of nanocomposite.

Many researches have been carried out to improve the interfacial compatibility between filler and polymer matrix by chemical modification to enhance the properties of composites[40-45], Professor Guo has done a lot of work in this area, for example, significant enhancements (i.e., 104.2%, 100.2%,and 78.3%) of interfacial shear strength (IFSS), interlaminar shear strength (ILSS), and flexural properties were achieved in the carbon fiber epoxy composites with triazine derivatives functionalized graphene oxide modified sizing agent[40].The IFSS of dopamine modified aramid fiber (AF)/epoxy composites was increased by 34% after grafting amino graphene oxide[42]. Therefore, the modified nano-filler grafted onto the fiber surface can significantly improve the performance of the composite. Nevertheless, the methods to significantly further improve the conductivity of nanocomposites above the percolation threshold are rarely reported. In order to overcome the electrical performance limitation of self-assembled conductive networks, a novel method of forced assembly was used for the condition where the packing concentration cannot further improve the conductivity of the composite [26,46-48], which aims to significantly reduce the gap between conductive fillers by forced compression because the flow performance of polymer is much higher than that of fillers. For example, the electrical conductivity of PDMS/ SCF composites prepared by the forced assembly method was effectively enhanced 1-5 orders of magnitude [26], Furthermore, the conductivity of PDMS/SCF composite can be further improved by more than 2 times by addition of nanoscale fillers at above the percolation threshold of SCF after simply forced compression [46].

In this work, a new technology, Spatial Confining Forced Network Assembly, issued SCFNA, aims to overcome the restriction on electrical performance of self-assembled conductive networks. The underlying mechanism of SCFNA method is to forced-compress the bulk density of the conductive network, accomplished by excluding the insulating polymer materials out of the conductive network and narrowing the distance between the adjacent nano-fillers. Based on the synergistic effect of micron and nanoscale fillers when preparing CPCs with an excellent electrical property, short carbon fiber (SCF) of 1-2 mm in length is selected as micron fillers to construct a conductive skeleton, Few-Layer graphene (Gr) or carbon nanotubes (CNT) is selected as nanoscale fillers. According to our previous research [26,46], the percolation threshold values of PDMS/SCF,

PDMS/CNT and PDMS/Gr(few-layer) composites prepared by SCFNA are 0.15 wt%, 0.1 wt% and 0.35 wt%, respectively. PDMS/SCF composites with 2 wt% SCF prepared by SCFNA method shows a relatively high DC electrical conductivity of over 100 S/m and a maximum tensile strength of 3.6±0.2 MPa. The increase of carbon fiber content leads to a rapid decrease in the mechanical properties of the composites, while the electrical conductivity is not significantly improved. Therefore, we set the content of carbon fiber as 2 wt% to research the effect of forced assembly on the properties of nanocomposites by changing the content of nanoscale fillers of CNT (from 1wt% to 4 wt%) or Gr from 0.5 wt% to 4 wt% and the assembly thickness of nanocomposites. As a consequence, the SCFNA method is capable of further promoting the electrical conductivity of nanocomposites when the nanoscale fillers loading level reaches or even exceeds the percolation threshold. Especially under the condition of relatively high filler concentration, the electrical conductivity enhancement effect is more significant, that is contrary to the classical percolation theory. Besides, we provide a comprehensive set of experimental data for investigating the compression-induced enhancement in electrical percolation and mechanical properties of flexible polydimethylsiloxane-based nanocomposites caused by the SCFNA method. A compression-induced percolation threshold was observed at approximately 0.3-0.5 mm thickness of composites samples when the addition of nanoscale fillers was higher than the concentration-induced electrical percolation, leading to PDMS nanocomposites characterized by not only super excellent electrical conductivity but also mechanical flexibility. The better mechanical properties of PDMS/2wt%SCF-2wt%Gr composites than pure PDMS indicated that SCFNA method not only can significantly improve the electrical properties of composites but also avoid reduction of mechanical properties when loading relative high fillers.

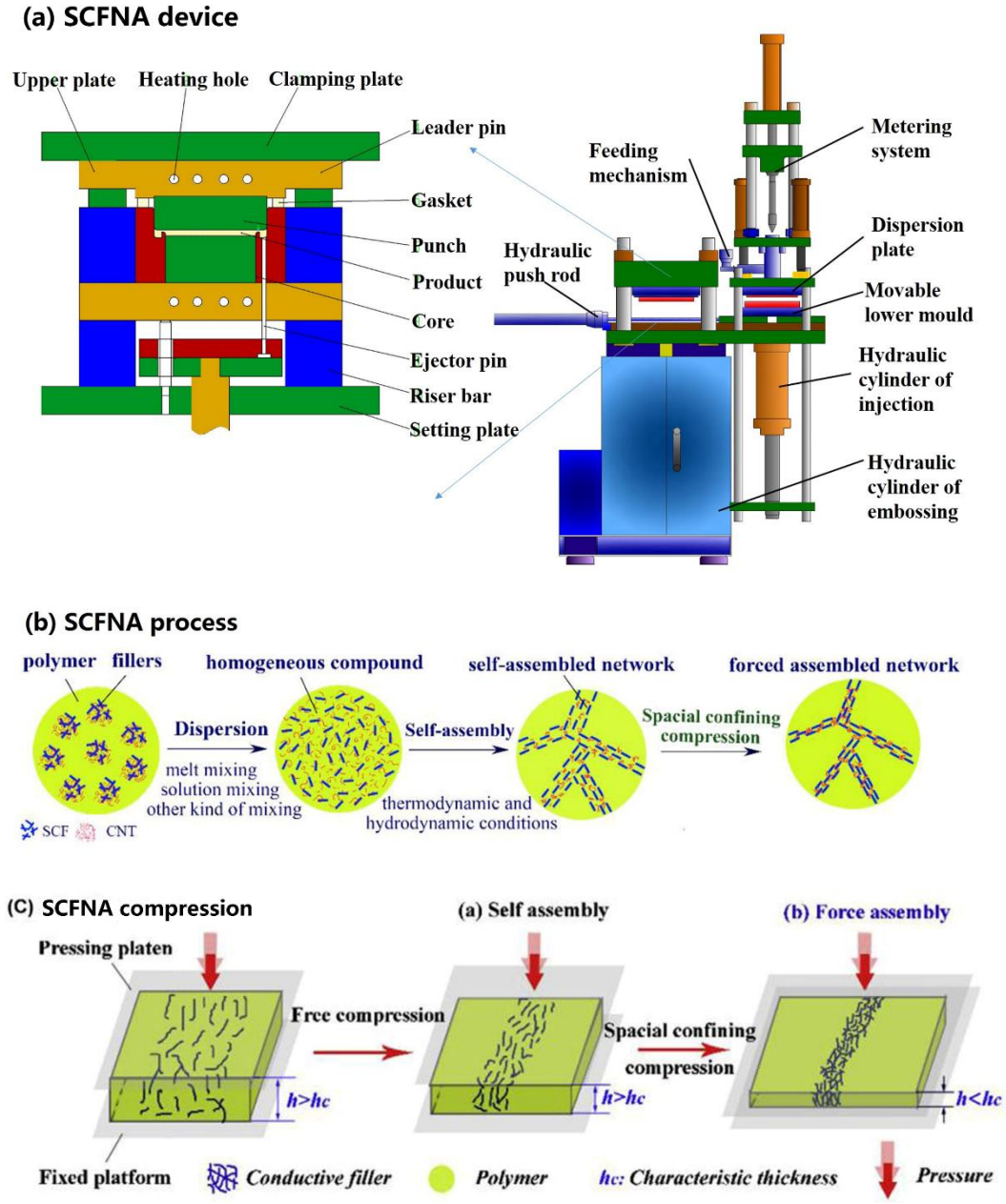
2. Experimental Section

2.1. Materials

PDMS with a trade name of SYLGARD 184 (DOW CORNING, USA) was adopted as a flexible polymer matrix. It consists of A and B components and is used in a 10:1 ratio. Diffirent kinds of conducting fillers of short carbon fibers (SCF), Few-Layer graphene (Gr), carbon nanotubes (CNT) were used as conductive phase filling materials. Graphene and CNT were bought from Sixth Element Material Technology, China and SCF was provided by Toray, Japan. The size of CNT is about 25 nm diameter and 20 μm length observed by scanning electron microscope(SEM). SCF and Gr is about 7 μm in diameter and 1-2 mm in length, 1.5 nm in thickness and 20 ~40 μm in width, respectively. The electrical conductivity of CNT, Gr and SCF are correspondingly 1.1×10^4 S/m, 1.0×10^5 S/m and 1.6×10^4 S/m.

2.2. PDMS-based Nanocomposites Preparation

Scheme (a) shows the forced assembly device and the compressing mold used to prepare the PDMS nanocomposites and form the forced assembled network structure. And their specific parameters are shown in our previous research work [46]. A conical twin-screw compounder of HAAKE MiniLab was used to prepare a homogeneous compound of PDMS and fillers. Firstly, the PDMS with 2 wt% SCF was mixed in HAAKE MinLab mixer for 5 min at a rotaional speed of 60 rpm and a barrel temperature of 20 °C. Secondly, CNT at weight ratios of 1, 2, 3, 4 wt% or Gr at weight ratios of 0.5, 1, 2, 3, 4 wt% was added into the PDMS/ 2wt% SCF compound to prepare PDMS/SCF-CNT or PDMS/SCF-Gr composites at the same processing conditions.



Scheme. (a) SCFNA device and the compressing mold used to prepare the PDMS nanocomposites and form the forced assembled network; **(b)** SCFNA process flowchart; **(c)** Schematic illustration of the SCFNA compression induced the filler dispersion from free packing to spatial confining assembly.

According to the steps shown in Scheme (b-c), firstly, the homogeneous compound of PDMS and fillers were compressed to 1.0 mm in the mould at 20 °C with a controled speed. The first step

called free compression aims to build a self-assmbly filler network in PDMS. Then the self-assembled network as shown in Scheme (c) were forced to assemble to 0.4, 0.3, 0.2, and 0.1 mm, respectively. The forced compression would finish after the sample thickness (h) was below a critical thickness (h_c ≈ 0.3～0.5 mm) in this work, Finally, the compounds were cured at 120 °C for 15 min.

2.3. Characterization

A Video Measuring System JTVMS-1510T (Dongguan JATEN Precision Instrument Co., LTD., China) and A Hitachi S4700 scanning electron microscopy (SEM) were used to investigate the morphology evolution of conducting filler network by SCFNA in PDMS. The microscopic size of nanometer fillers was observed by a Hitachi NX2000 transmission electron microscope(TEM). An electrical performance testing system of Keithley 4200-SCS (America) was used to measure the conductivity of the nanocomposite sheets. A mechanical performance testing device of UTM-1422, from Chengde Jinjian Testing Instrument Co., Ltd was used to obtain the tensile curve of the PDMS nanocomposites. The size of the PDMS composite sheets is 30 mm × 15 mm× 0.1 mm, 30 mm × 15 mm× 0.2 mm, 30 mm × 15 mm× 0.3 mm, 30 mm × 15 mm× 0.4 mm, respectively. All measurements were carried out at ambient conditions.

3. Results and Discussion

3.1. Compression-Induced Electrical Percolation of PDMS Nanocomposites

A compression-induced percolation threshold was found when the thickness of polydimethylsiloxane (PDMS) nanocomposite samples was reduced via a Spatial Confining Forced Network Assembly (SCFNA) process from 1.0 mm to 0.1 mm. The critical thickness (h_c) is relative to a volumetric strain when it reached a critical value ε_c or under a critical pressure P_c [49], as expressed in Eq.1 and Eq.2:

$$\varphi_c = \frac{\varphi_0}{1 - \Delta P_c} \quad (1)$$

$$\varepsilon_c = 1 - (\frac{\varphi_0}{\varphi_c}) \quad (2)$$

Where ΔP_c is the pressure increment (P- P_c) when the percolation transition changes from φ_0 to φ_c.

The relationship between the assembly thickness and the DC electrical conductivity of PDMS nanocomposites is plotted in Figure 1ab. As revealed in these curves, the compression-induced percolation transition occurred at about 0.3-0.5 mm thickness of samples when the addition of nanoscale fillers increased from 0.5 wt% to 4 wt% above the concentration-induced electrical percolation. In details, h_c is about 0.4mm-0.5mm and 0.3mm-0.4mm of PDMS/SCF-CNT and PDMS/SCF-Gr composites, respectively. With the nano-filler content increase, h_c slowly increased (the reason was shown in next paragraph). Take the case of PDMS/2wt%SCF-CNT or PDMS/2wt%SCF-Gr nanocomposites as an example, the electrical conductivity experienced a mild increase when the sample was thicker than h_c and shown a sharp enhancement when the thickness was thinner than h_c.

These phenomena indicated that a new concept of the compression-induced percolation transition can be proved, that is, a forced network with a high compression ratio. The continuous enhancement of electrical conductivity caused by the further reduction of the sample thickness was substantial until it equaled to 0.1 mm, from original 68.1 S/m (at 1 mm) up to 317 S/cm for PDMS/2wt%SCF-0.5wt%Gr, and the PDMS/2wt%SCF-1wt%CNT composite undergone the increase of the electrical conductivity from 49 S/m to 199 S/m similarly. When the thickness of the PDMS/2wt%SCF-4wt%CNT or PDMS/2wt%SCF-4wt%Gr nanocomposites was compressed from initial value to 0.1 mm, their conductivity enhanced considerably form 59.5 S/m to 487 S/m, 74.2 S/m to 394 S/m, enhanced 7.2 and 4.3 times, respectively. However, with the increase of the CNT concentration from 1 wt% to 4 wt% above the percolation threshold, the conductivity of PDMS/2wt%SCF-CNT nanocomposite (1 mm) presented a slight increase tendency from 49.0 S/m to 59.5 S/m, only increased by 21.4%, as shown in Figure 1e. This indicates that, the ultimate conductivity of nanocomposites prepared by conventional blending method is considered to be independent of the filler loading when the concentration-induced percolation threshold is much lower than the packing concentration), i.e., the curves representing the electrical conductivity variation becomes gradual even though the continuous growth in filler concentration. Nevertheless, SCFNA compression could be applicable to assemble a closer-compact conducting network, and obtain an excellent conductive performance without any increase in filler concentration. It is particularly viable in cases where the conductivity of CPCs can be further increased by a compression-induced percolation transition even though the filler concentration reaches saturation. Such phenomenon can be seen from the Figure 1bf as for PDMS/2wt%SCF-Gr nanocomposites, and all detailed measurements are listed in Table 1-2.

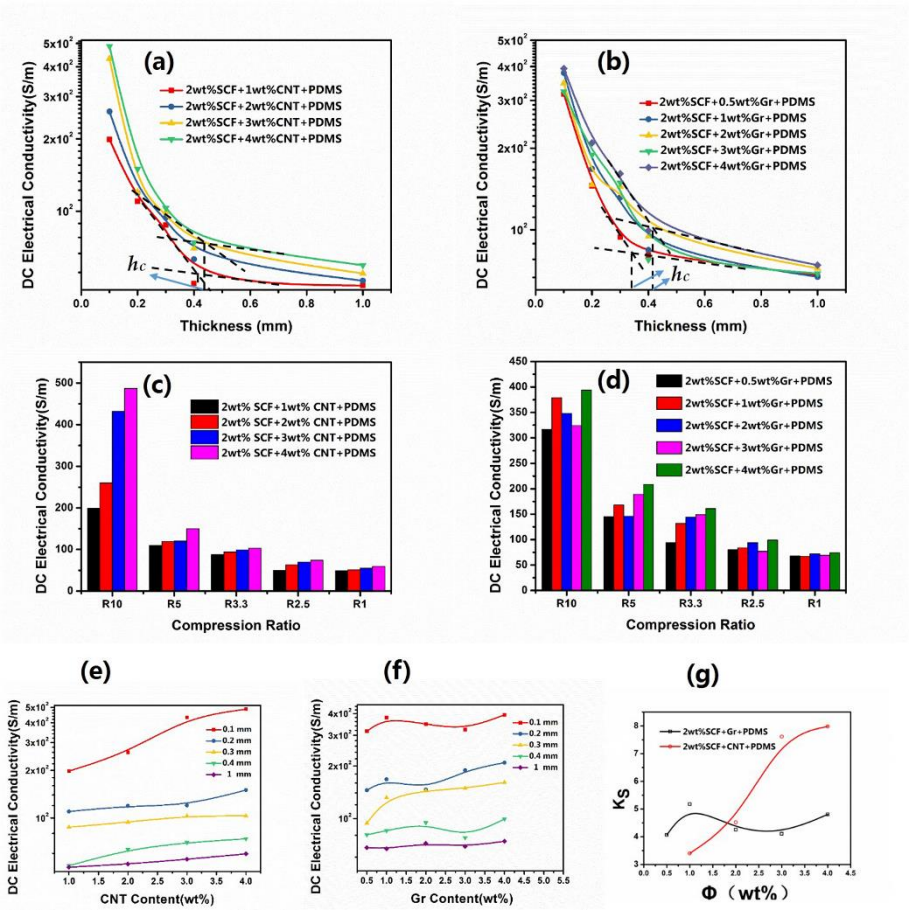


Figure 1. (**a-b**) The relationship between the assembly thickness and the DC electrical conductivity of PDMS nanocomposites; (**c-d**) The relationship between the compression ratio (*R*) and the conductivity of PDMS nanocomposites (**e-f**) effect of nano-filler content on the DC electrical conductivity of PDMS nanocomposites; (**g**) the strain sensitivity *Ks* of the conductivity of the PDMS nanocomposites at different nanoscale filler contents.

The compression ratio(R) is defined as the initial thickness over the thickness of the nanocomposites after forced assembly. R were 2.5, 3.3, 5, 10 when the forced assembly thickness was 0.4, 0.3, 0.2, 0.1 mm, respectively. As shown in Figure 1cd, the curves show the effect of R on the electrical conductivity of the PDMS nanocomposites. As presented in Figure 1c, the conductivity of the PDMS/2wt%SCF-CNT composites is generally increased with the increase of R. Taking R=10 as an example, the conductivity of PDMS/2wt%SCF-CNT composites are enhanced by 3.06, 4.07, 6.85, 7.18 times with the corresponding addition of 1, 2, 3, 4 wt% CNT concentration. It shows the more addition of CNT, the better electrically conductive property of the composites at the same compression ratio, which means compression-induced electrical percolation appeared in advance. This is because the gaps between the adjacent fillers in the network that makes up the conductive pathways are smaller when adding more nano-fillers. It also explained why h_c was larger at high nano-filler content as shown in Figure 1ab. Similar to CNT adopted as the nano-filler, the usage of Gr added into PDMS/SCF mixture remarkably improved the conductivity as well along with the thickness reduction as shown in Figure 1d. In contrast, the combination of one-dimensional CNT and micro-scale SCF has better synergistic effect, as CNTs are more easily to fill the gaps between the SCF networks compared with two-dimensional Gr.

In order to investigate the relationship between the electrical conductivity and the compression thickness of composite samples, the strain-sensitivity coefficient *Ks* is plotted against the filler content according to Eq. 3, and shown in Figure 1g.

$$K_S = \frac{d\sigma}{\sigma} / \frac{dh}{h} \tag{3}$$

Where *dh*/*h* is the thickness strain during the SCFNA process, $(\frac{d\sigma}{\sigma})$ is a relative increment of the conductivity.

It can be seen form Figure 1g, the forced assembly thickness has a great influence on *Ks*. With the CNT concentration increased from 1 to 4 wt%(over concentration-induced percolation threshold), the *Ks* increased from 3.4 to 7.98, indicating a further electrical conductivity enhancement by SCFNA compression. Especially under the condition of relatively high CNT filler concentration, the electrical conductivity enhancement effect is more significant, that is contrary to the classical percolation theory.

In contrast, when the Gr content increased from 0.5 to 4 wt%, the *Ks* increased slightly from 4.07 to 4.8. There was an intersection at about 2 wt% filler content as shown on the curve, which indicated that the CNT filler played a more effective role in increasing electrical properties of PDMS/SCF mixture than Gr when its loading content was more than about 2 wt%.

Table 1. Comparison of electrical conductivity of PDMS/2wt%SCF-CNT nanocomposites at different assembly thickness and CNT concentration. The assembly thickness values of PDMS-based nanocomposites were 0.1, 0.2, 0.3, 0.4, 1 mm, the CNT filler content is 1, 2, 3, 4 wt%, respectively.

CNT (wt%)	DC Electrical Conductivity of PDMS/2wt% SCF-CNT (S/m)				
	0.1 mm	0.2 mm	0.3 mm	0.4 mm	1 mm
1	199	110	87.6	50.1	49.0
2	260	119	94.2	63.4	51.3
3	432	120	99.1	70.2	55.0
4	487	150	103	74.0	59.5

Table 2. Comparison of electrical conductivity of PDMS/2wt%SCF-Gr nanocomposites at different assembly thickness and CNT concentration. The assembly thickness values of PDMS-based nanocomposites were 0.1, 0.2, 0.3, 0.4, 1 mm, the Gr filler content is 0.5, 1, 2, 3, 4 wt%, respectively.

Gr (wt%)	DC Electrical Conductivity of PDMS/2wt% SCF-Gr (S/m)				
	0.1 mm	0.2 mm	0.3 mm	0.4 mm	1 mm
0.5	317	145	94.0	80.5	68.1

1	379	168	132	85.1	67.3
2	348	146	144	94.5	72.0
3	324	189	149	77.5	69.4
4	394	209	161	99.2	74.2

3.2. Compression-Induced Enhanced Mechanical Properties of PDMS nanocomposites

Table 3. Mechanical properties of PDMS nanocomposites at varied thickness.

PDMS nanocomposite			Maximum tensile strength (MPa)	Elongation at break (%)
Thickness	SCF	Nano-filler		
0.2mm	0	0	4.5 ±0.1	110 ±2
0.2mm	2wt%	0	3.6±0.2	91±4
0.1mm	2wt%	2wt% CNT	4.3 ±0.1	107 ±2
0.2mm	2wt%	2wt% CNT	4.1 ±0.2	102±4
0.3mm	2wt%	2wt% CNT	4.0±0.1	98±1
0.4mm	2wt%	2wt% CNT	3.8±0.1	95±1
1mm	2wt%	2wt% CNT	3.7±0.1	93±1
0.1mm	2wt%	2wt% Gr	5.2±0.2	114±4
0.2mm	2wt%	2wt% Gr	5.0±0.2	109±4
0.3mm	2wt%	2wt% Gr	4.8±0.2	107±4
0.4mm	2wt%	2wt% Gr	4.7±0.1	105±3
1mm	2wt%	2wt% Gr	4.5±0.2	104±3

The variations of mechanical properties compared between pure PDMS, PDMS/SCF composite and PDMS nanocomposites versus varied sample thickness, including the maximum tensile strength and elongation at break, are presented in Figure 2. As revealed in these curves, the nanocomposites with less thickness had higher maximum tensile strength and elongation at break than that with greater thickness. For example, the maximum tensile strength of PDMS-CNT nanocomposite is enhanced by up to 16.2% from 3.7 ± 0.1 MPa to 4.3 ±0.1 MPa as the thickness of samples were compressed from 1.0 mm to 0.1 mm. As for PDMS/2wt%SCF-2wt%Gr composites, the improvement of maximum tensile strength is by 15.6%, from 4.5 ± 0.2 MPa to 5.2 ±0.2 MPa. The enhanced mechanical properties induced by SCFNA compression can be ascribed to a more tightly oriented SCF (or Gr) and CNT interconnection network (referring to Figure 3-4) after forced compression. The detailed information about mechanical properties comparison for pure PDMS and PDMS composites for various thickness are listed in Table 3. The results demonstrated that maximum tensile strength and elongation at break were obviously dependent on the type of filling materials and blending ratio of the polymers. Compared with the maximum tensile strength of 0.2 mm PDMS/0.2wt SCF (3.6 ± 0.1 MPa), the addition of CNT or Gr enhanced the tensile strength and elongation at break of the composites. This discrepancy can be attributed to the mechanical reinforcement effect of nano-fillers. Moreover, the results illustrated that Gr performed a better mechanical reinforcement effect than CNT in terms of the mechanical properties of composites. The interfacial interaction between Gr sheets and PDMS is much stronger than that between one-dimensional CNT or SCF as its larger specific surface area. The addition of CNT and SCF slightly weaken the tensile strength and elongation at break of composites in comparison with the maximum tensile strength of 0.2 mm pure PDMS (4.5 ± 0.1 MPa), causing the PDMS/2wt%SCF-2wt%CNT composites become more vulnerable to tensile damage. This phenomenon, in particular, took place for thicker samples condition (such as 3.7 ±0.1 MPa for 1 mm thickness), while the reduction was negligible under thinner samples condition (such as 4.3 ±0.1 MPa for 0.1 mm thickness and 4.1 ±0.1 MPa for 0.2 mm thickness). Nevertheless, comparing with pure PDMS, the better mechanical performances of PDMS/2wt%SCF-2wt%Gr composites represented that SCFNA compression method was capable of not only providing the better electrical performance but also avoiding reduction in terms of mechanical characteristics when loading relative high fillers.

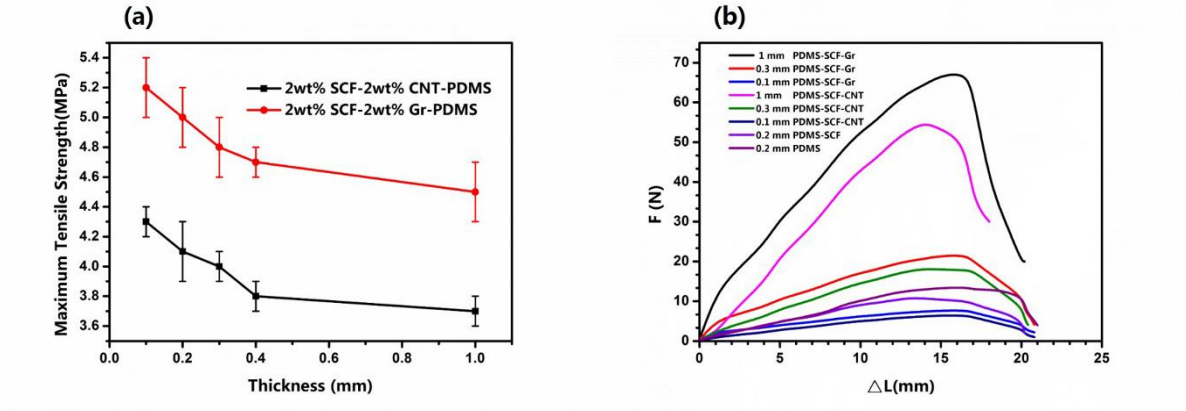


Figure 2. (a) The relationship between the assembly thickness and the mechanical properties of PDMS nanocomposites;(b)the tensile curve of PDMS nanocomposites、 pure PDMS and PDMS/SCF composite at varied thickness (Gr content: 2 wt%, CNT content: 2 wt% SCF content: 2 wt%), F is the tensile force, ΔL is the elongation of the composites under a tensile force.

3.3. Characterisation of the Morphology Evolution of Conducting Filler Network by SCFNA in PDMS

In order to construct a pathway in the insulating PDMS matrix by utilizing conductive fillers, a fresh approach of SCFNA compression was applied to shrink the gap between adjacent filler particles, leading to a more compacted electrical conductive network and a resultant more enhanced electrical conductivity polymer composites. The underlying mechanism of SCFNA method is to introduce a mechanical delivered additional interaction. Herein, there exists a characteristic diameter (known as the thickness of compression-induced percolation transition), less than which a noteworthy densification of the network threads would be obtained. Besides, an inner-connection network might be formed due to the gap-filling effect of the additional nanoscale fillers employed in such as CNT or Gr on the conductive network composed of short carbon fibers. Therefore, both the electrical conductivity and mechanical properties of the nanocomposites could be strengthened, which is urgently required for polymer engineering involved in design for highly sensitive flexible sensor technology project.

In terms of the morphology evolution of PDMS/SCF/nano-filler composites, the conducting filler networks within the cross-section of both PDMS/2wt%SCF-2wt%CNT and PDMS/2wt%SCF-2wt%Gr nanocomposites are presented in Figure 4-5, respectively, and figure 3 shows SEM of short carbon fiber(SCF). The pictures in Figure 4ad revealed that, as the consequence of free compression, a homogeneous dispersion of CNT was observed within the environment of PDMS and a self-assembly network was formed at this phase accompanied with the compacted thickness equal to 1 mm. Most CNTs (referring to the circle of Figure 4d) were more likely to disperse in PDMS rather than in the neighborhood of SCF network. Under the period of free compression, filler particles could move freely in horizontal and vertical directions and yet the gap between the adjacent CNT fillers couldn't be reduced to yield a sufficient close distance. According to the cross-sectional images represented in Figure 4be, however, because of the treatment of the second stage issued as the forced compression, there came a forced-assembly network and the thickness was condensed to 0.2 mm. Some CNTs were still scattered under the frame of PDMS but some were compelled to proximate to the SCF network (referring to the circle of Figure 4e). Furthermore, with the forced compression continues, as shown in Figure 4cf, a selective dispersion of most CNT coupled with agglomerated phenomenon in the vicinity of the SCF network was observed when the thickness was compressed to 0.1 mm. Herein, the quantity of CNT dispersed in PDMS environment became minor, and majority of CNTs gave their priority to approach the SCF network, thus agglomerating to construct an interconnection network. The distribution pattern of synergetic combined fillers of SCF and CNT can be clearly observed from the overview of the PDMS/2wt%SCF-CNT composite surface with a thickness of 0.1 mm in Figure 6.

During the process of forced compression, filler particles' movement was restricted in horizontal but free in vertical direction (referring to Scheme c), and the average distance between CNT filler network was reduced, meaning that a more compacted conductive network was formed. That is why forced assembly is beneficial to the synergistic effect of micron and nanoscale fillers, SCFNA process is a way to superimpose the applied force field and the self-assembly force of the filler in a positive way, through forced assembly, nano-fillers are more likely to selectively distribute in the vicinity of micron conducting networks to form a combinatorial effect as shown in figure 4cf, thus results in a secondary compression-induced electrical percolation of the nanocomposite. Therefore, the traditional electrical conductivity of nanocomposites could be considerably enhanced by a compression-induced percolation transition, i.e. SCFNA compression. To summarize, the self-assembly network could be converted to a forced-assembly network by SCFNA compression, accompanied with phenomena of electrical conductivity optimization and mechanical properties improvement once the sample was compressed to a thickness of less than h_c.

Likewise, the dispersion of conductive fillers in PDMS/2wt%SCF-2wt%Gr nanocomposites was shown, with the thickness of 0.1 mm in Figure 5ab and 1 mm in Figure 5cd. As represented, Few-Layer graphene sheets were primarily separated inside the PDMS matrix rather than surrounded with the carbon fiber network when the thickness of nanocomposites was free-assembly compressed to 1 mm. This implied that the synergy between Gr and SCF in the conductive network is relative weak. Nevertheless, after nanocomposites experienced force compression condensed to 0.1 mm thickness, some graphene sheets shifted from the surrounding area of PDMS to attaching to the SCF network. Noted that, in comparison with the 0.1 mm thickness of PDMS/2wt%SCF-CNT nanocomposites, the PDMS/2wt%SCF-Gr nanocomposites with 0.1 mm thickness performed better electrical conductivity in low nano-filler concentration (such as 1% and 2%) but poorer in high nano-filler concentration (such as 3% and 4%). Such a phenomenon seemed to be deviate from the theoretical knowledge, i.e. Gr is more conductive than CNT. This can be ascribed to the agglomerates of graphene sheets. That is to say, the agglomerated graphene loses the high-performance electrical conductivity of single or Few-Layer graphene. In addition, one-dimensional (1D) carbon fibers combined with one-dimensional (1D) carbon nanotubes are easier to fill and twine with each other to form a tighter conductive network than one-dimensional (1D) carbon fibers combined with two-dimensional (2D) few-layer graphene sheet, that is why the synergistic effect of graphene content on the conductivity of the PDMS nanocomposites is not as significant as that of carbon nanotubes content.

As shown in Figure 7a, the connection of the two adjacent conducting fillers formed a conductive path, where I is the current and U is the voltage. Here, the resistance of the polymer sandwiched between fillers was assumed to be related to the distance between these two adjacent fillers, meaning that the smaller the gap, and the lower the resistance. According to Ohm's Law, the larger current of electrical circuit indicates the smaller electrical circuit resistance. Two types of conduction pathways are illustrated in Figure 7bc, for PDMS/SCF/nano-filler composites at the thickness of 1 mm and 0.1 mm, respectively. As presented in Figure 7b, for the sample thickness of 1 mm, the nano-fillers were dispersed in PDMS homogeneously maintaining certain distance with SCFs. Under this condition, most nano-fillers acted as series resistance between the adjacent SCFs and few ones served as parallel resistance. While, for the sample thickness of 0.1 mm displayed in Figure 7c, the nano-fillers were dispersed selectively in vicinity of the SCF network to build close-connection with the adjacent SCFs, majority of which undertook the duties as parallel resistance between the adjacent SCFs rather than series resistance. Therefore, the ultimate resistance of circuit in Figure 7c (0.1mm PDMS/SCF-nano-filler composite) is much smaller than that of circuit in Figure 7b (1mm composite), indicating that in comparison with composites with greater thickness, thinner ones provided better performance on electrical conductivity.

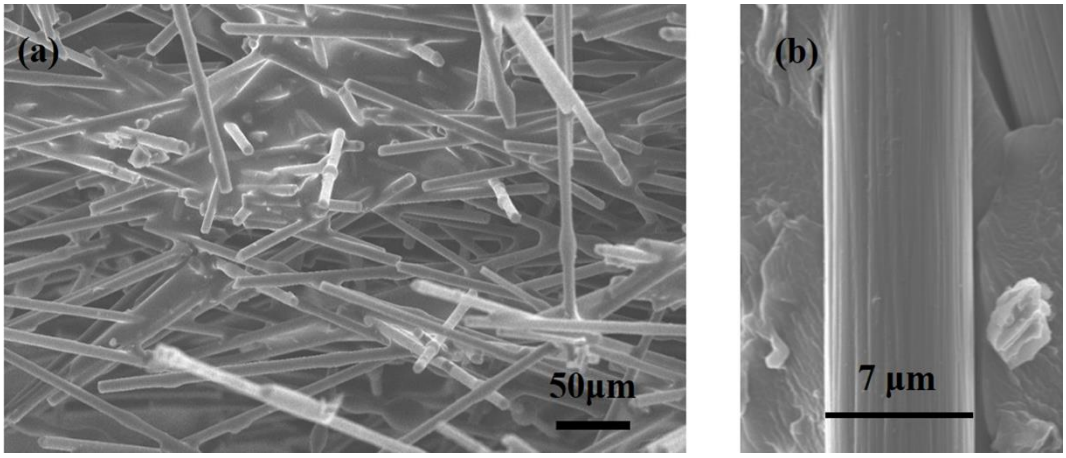


Figure 3. SEM of short carbon fiber(SCF).

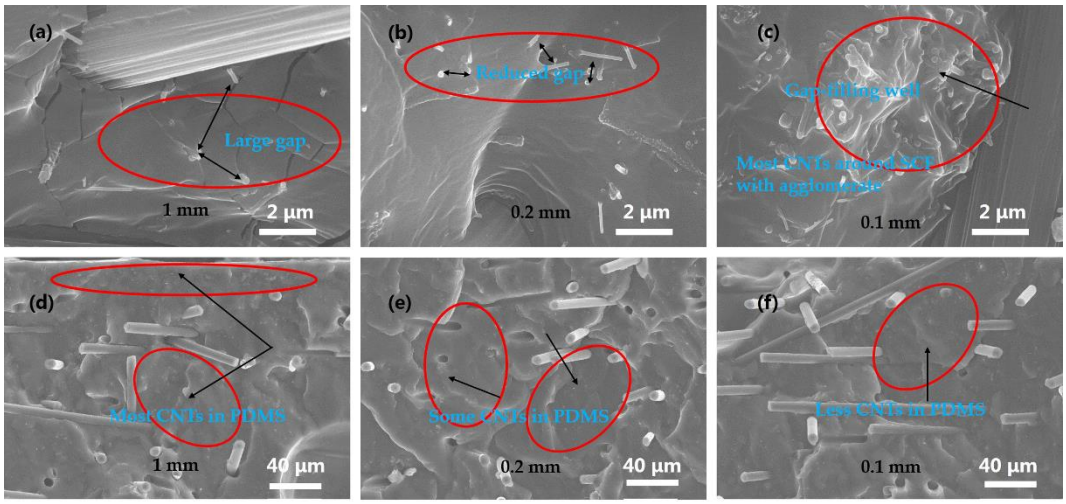


Figure 4. Dispersion of CNT network in PDMS/2wt%SCF-2wt%CNT nanocomposites: (a,d) SEM of uniform dispersion of CNT in PDMS when the thickness of composite is 1 mm; (b,e) SEM of selective dispersion of CNT around the SCF network after forced compression to the thickness of 0.2 mm; (c,f) SEM of selective dispersion of CNT with agglomerated phenomenon around the SCF network after forced compression to the thickness of 0.1 mm.

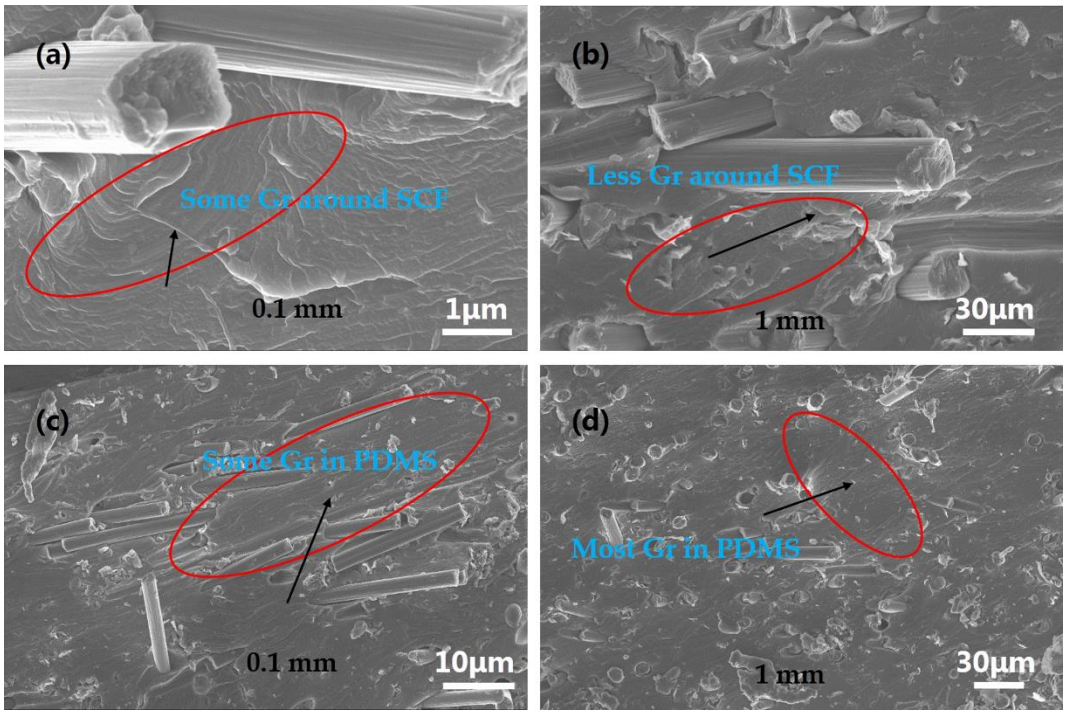


Figure 5. Dispersion of Gr network in PDMS/2wt%SCF-2wt%Gr nanocomposites: (a,c) SEM of selective dispersion of Gr around the SCF network after forced compression to the thickness of 0.1 mm; (b,d) SEM of homogeneous dispersion of Gr in PDMS after free compression to the thickness of 1 mm.

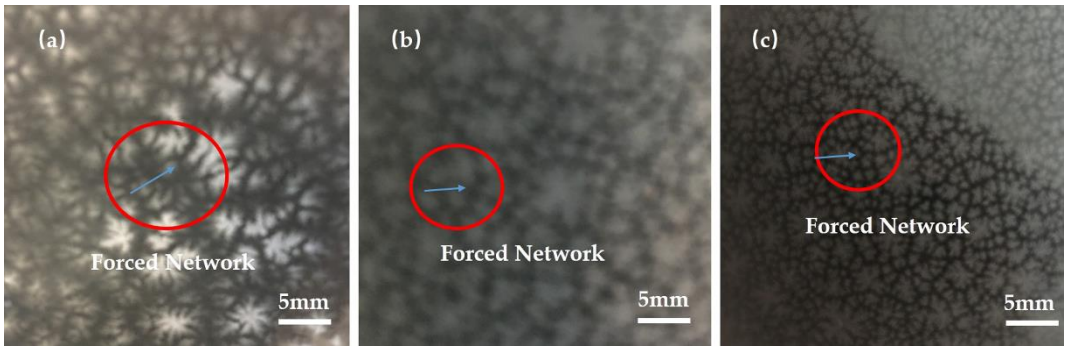


Figure 6. Overview of the PDMS/2wt%SCF-CNT composite samples with a thickness of 0.1 mm: (a) 1wt% CNT; (b) 2wt% CNT; (c) 4wt% CNT. (by digital camera)

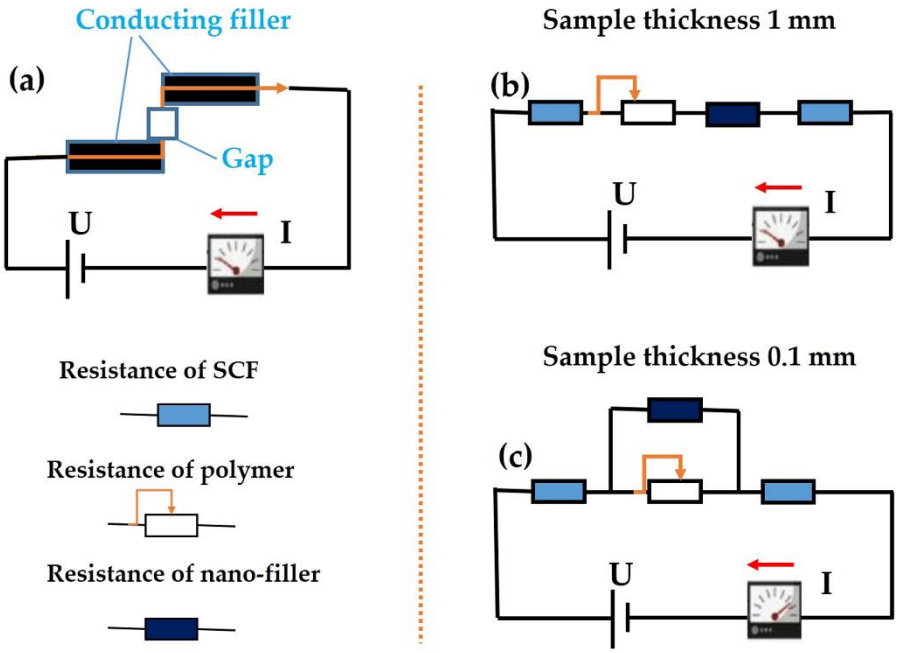


Figure 7. Model of conductive pathway consisted of the adjacent filler in polymer matrix. Principle of resistance in conductive pathway in PDMS nanocomposites with the thickness of (b) 1 mm and (c) 0.1 mm.

4. Conclusions

In this work, we investigated compression-induced electrical percolation and enhanced mechanical properties of flexible polydimethylsiloxane-based nanocomposites by the forced assembly method. SCFNA process is a way to superimpose the applied force field and the self-assembly force of the filler in a positive way. Through forced assembly, nano-fillers are more likely to selectively distribute in the vicinity of micron conducting networks to form a combinatorial effect, especially for the one dimensional linear micro-nano fillers combination system, thus results in a secondary compression-induced electrical percolation of the nanocomposite. It is beneficial to the synergistic effect of micron and nanoscale fillers and enhances the continuity of the conductive network in the polymer matrix, it has been proved that the electrical conductivity of nanocomposites can be greatly improved. A compression-induced percolation threshold occurred at about 0.3-0.5 mm thickness of samples when the addition of nanoscale fillers increased from 1 wt% to 4 wt% above the concentration-induced electrical percolation, resulted in ultra-high conductivity and mechanical flexible PDMS-based nanocomposites. Meanwhile, the better mechanical properties of PDMS/2wt%SCF-2wt%Gr composites than pure PDMS indicated that SCFNA method not only can significantly improve the electrical properties of composites but also avoid reduction of mechanical properties when loading relative high fillers. This novel processing method will greatly promote the application of CPCs in the areas of electrodes、smart wearable devices and electromagnetic shielding.

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